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Application of Structure Property Relationships to Develop Seven Segmented Polyurethane Adhesives

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Application of Structure-Property Relationships to Develop Seven Segmented Polyurethane Adhesives

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ABSTRACT

Seven polyurethane adhesives have been developed to meet a series of design requirements for weapons. These adhesives, designated Halthanes, were synthesized because of OSHA restrictions on the use of the curing agent methylene bis(2- chloroaniline) with the objective of meeting qualitative design requirements imposed by our

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engineers. Four of the Halthanes were made from LLNL-developed 4,4'-methylene bis(phenylisocyanate) terminated prepolymers cured with a blend of polyols; three were made from an LLNL-developed prepolymer terminated with Hylene W and cured with aromatic diamines.

The design requirements for various adhesive properties were subdivided based on chemical and macromolecular structure of the adhesive and its components so that structure-property relationships could be applied. Changes in the structure of prepolymer, curing agent and accelerator were made to achieve initial viscosities in the range of 6 and 40 Pa-sec, and working times of from 4 to 24 hours. The structure of the polymer/substrate interface was used to obtain adhesive strengths of from 8-14 MPa at room temperature. The morphology and concentration of the hard and soft segments were used to control the modulus and elasticity of these segmented polyurethanes. Based on these structure-property relationships we have produced seven polyurethane adhesives that bond rapidly and well, have low to intermediate modulus over a wide temperature range, and appear to be reasonably compatible with other components.

INTRODUCTION

Restrictions imposed by the Occupational Safety and Health Administration on the use of methylene bis(2-chloroaniline) (MOCA) were the impetus to development of alternative adhesives for Adiprene L-100/MOCA. These new adhesives would be required to meet seven qualitative design requirements imposed by LLNL design engineers. The physical properties based on the design requirements were subdivided into four structure-property categories related to the chemistry and molecular architecture of segmented polyurethanes.[1] Using these structure-property relationships as guidelines, several polyurethane adhesives were synthesized, and subsequently characterized to determine how well they satisfied the original design requirements. With advances in weapon design, new adhesive applications required different physical properties. Again following structure-property relationships seven polyurethane adhesives were selected to meet a wide variety of applications.

These segmented polyurethane adhesives needed to meet the following seven design requirements:

2. Working time of at least 1 hour.

3. Cure time such that the adhesive has sufficient bond strength to permit removal of tools and clamping fixtures after 16 hours or, for some applications, 4 to 8 hours.

4. Adhesive tensile strength to metals and high explosives of approximately 7 MPa over the temperature range from -50 to 70°C. For some applications at least 10 MPa breaking stress is desirable.

5. Low modulus and some elasticity over the -50 to 70°C temperature range. For one application the adhesive must not flow at 150°C.

6. Compatibility with high explosives and other weapons components.

7. Service life of 20-25 years under military operating conditions.

The design requirements for the segmented polyurethane adhesives fall into four structure-property categories. Requirements 1-3 for low initial viscosity, 1 hour pot life;

and 16 hour cure time are controlled by the prepolymer and curing agent chemistry. The structure of the polymer/substrate interface determines the adhesive strength (Requirement 4). The molecular architecture of the hard and soft segments in the final polymer determines the modulus and elasticity of the adhesive (Requirement 5). The use-life and compatibility with other weapons components (Requirements 6 and 7) are directly related to both the segmental structure of the polymer and the particular use environment of the adhesive. Based on these structure-property relationships we have produced seven polyurethane adhesives that bond rapidly and well, have low to intermediate modulus over a wide temperature range, and appear to be reasonably compatible with other components.

COMPOSITION - CURE RELATIONSHIPS

Our adhesive formulations were adjusted so that the structure of the prepolymer, curing agent, and accelerator produced viscosities, working times, and cure rates close to those specified in the design requirements. Three types of adhesives were developed and called Halthanes. The 73-series Halthanes contained 4,4'-methylene bis(phenyl isocyanate) (MDI)-butanediol hard segments. The 87- and 88- series Halthanes contained 4,4'-methylene bis(cyclohexyl isocyanate) (HMDI)-aromatic diamine hard segments. All adhesives contained poly(tetramethylene glycol) soft segments.

The formulations of the prepolymers and curing agents of the four 73- series Halthanes are given in Table I. The 73-series prepolymers consist of low molecular weight oligomers with about 3 moles excess isocyanate. 73-14 and 73-15 are cured with only difunctional alcohols so that linear segmented polyurethanes are produced. Ferric acetylacetonate catalyst is added to 73-15 and 73-19 to accelerate the cure. The tetrafunctional alcohol N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine (quadrol) was used to crosslink the adhesive, increase the cure rate, and decrease the working time in 73-18 and 73-19 adhesives.

The formulations of the prepolymers and curing agents of the 3 members of the 87- and 88-series Halthanes are given in Table II. The 87-1 prepolymer is cured with TONOX 60/40, a blend of 60% methylenedianiline and 40% m-phenylenediamine. The 87-2 and 88-2 prepolymers are cured with XU-205, a liquid mixture of substituted 4,4'-methylene bis(2-ethylaniline) and similar diamines containing one or no ethyl groups on the phenyl ring. The 88-prepolymer has a slightly higher concentration of diisocyanate.

The prepolymer and curing agent determine the viscosity, potlife and working time.[2,3] Figure 1 is a semi-log plot of the apparent viscosity (η) of the adhesive at constant shear rate and temperature with time (t). The higher viscosity of 73-18 compared to 73-14 is due to branching caused by the tetrafunctional quadrol. The addition of ferric acetylacetonate catalyst to 73-19 increases its cure rate and viscosity over that of the 73-18 adhesive.[4]

Changing the chemistry of the curing agent from diols of the 73- series to diamines in the 87- and 88- series results in more rapid formation of higher viscosity polyurea hard segments. Using different diamines changes the kinetics of the chain extension reaction as shown by comparison of the viscosity-time curves of 87-1 (TONOX 60/40) and 87-2 (XU-205). Changing the concentration of diisocyanate and diamine increases the concentration of hard segments and the initial viscosity of 88-2 above 87-2 (Figure 1). Other physical properties related to the chemical reactions during polymerization such as cure time, pot life, and working time, behave similarly to the viscosity.

ADHESION-POLYMER/SUBSTRATE INTERFACE RELATIONSHIPS

The adhesive strength of a polymer/substrate bond is determined by chemical and mechanical interactions at the polymer/substrate interface.[5] Figure 2 is a schematic representation of chemical adhesion due to hydrogen bonding to the metal oxide surface layer, van der Waal's interactions at the surface, and actual chemical reaction of the excess isocyanate with the metal oxide. Another contribution arises from mechanical adhesion represented in the figure by the flow of the adhesive into rough surfaces. The adhesive strength will also depend on the modulus of the adhesive and crack propagation at the interface.

The interrelationship between chemical and mechanical adhesion is extremely complex and not readily extractable from simple tests. Butt-tensile tests of the adhesives were made using degreased and chromic acid etched 28.68 mm diameter right cylinders of aluminum. The breaking stress as a function of cure time is shown in Figure 3 for 73-14, 73-18, and 87-1 adhesives cured and tested at room temperature. The best bond strength occurs in the highest modulus adhesive (87-1) indicating the importance of mechanical adhesion. The strength increases to a maximum, then drops to a minimum and finally levels off to some intermediate value. This behavior must be related to the complex nature of the chemistry at the adhesive-metal interface.

The butt-tensile strength as a function of temperature for 73-18, 73-19, and 88-2 adhesives (Fig. 4) also shows the importance of mechanical adhesion. The glass transition of soft segments in the 73- adhesives occurs at about -50°C whereas in the 87- and 88- adhesives it occurs at about -74°C. Thus the modulus of the 73- adhesives and also the butt-tensile strength increases more rapidly than the 87- and 88- adhesives causing the crossover in the 87- and 73- series butt-tensile strength curves that occurs at about -30°C.

MODULUS AND ELASTICITY-HARD AND SOFT SEGMENT ARCHITECTURE RELATIONSHIPS

The modulus and elastic properties of these segmented polyurethane adhesives are controlled by the concentration and chemical structure of the hard and soft segments, i.e., the polymer architecture.[6,7] Halthanes consist of low glass transition temperature phases called soft segments and high glass transition temperature phases called hard segments. Below the hard segment glass transition these domains act as temporary crosslinks and reinforcing fillers in the adhesive.

The modulus of the adhesive will change dramatically above and below the glass transition temperature of the hard, T_g(HS), and soft, T_g(SS), segments. Dynamic mechanical measurements as a function of temperature were made on all the Halthanes. The low temperature shear storage modulus (G') and shear loss modulus (G") are plotted as a function of temperature in Figure 5 for 73-14, 87-1, and 88-2 adhesives.

Since the 73- soft segments are composed of mostly 1000 molecular weight poly(tetramethylene glycol), they have higher T_gs (-50°C) than the 2000 molecular weight soft segments of the 87- and 88- adhesives (-74°C). Notice that the crossover in the shear storage modulus (G') for 88-2 and 73-14 occurs at about -45°C which is only slightly lower than the crossover for butt-tensile tests as a function of temperature (Fig. 4).

In amorphous linear segmented polyurethanes, like 73-14 and 73-15, above the hard segment glass transition temperature the polymer will flow since effectively the crosslinks have melted.[8] Urethanes with chemically crosslinked hard segments, such as 73-18 and 73-19, on the other hand, will remain elastomeric above the hard segment transition (see Fig. 6). Clearly, if the adhesives must function above T_g(HS), the chemically crosslinked polyurethanes are superior.

If T_g(HS) is higher than the maximum use temperature as in the 87- and 88- polyurea hard segments, linear adhesives will perform satisfactorily. However, for large differences between cure temperature and T_g(HS), incomplete reaction of the hard segments can occur. Incomplete curing causes a post-curing phenomena (Figure 7). As the polyurethane is heated, the mobility of the hard segments increases allowing further chemical reaction. This results in an increase in modulus because of the increasing extent of reaction in the hard segment prior to polymer flow above T_g(HS).

The modulus and elasticity of the rubber plateu between $T_g(SS)$ and $T_g(HS)$ depends on the chemical structure, concentration, and degree of microphase separation of the load bearing hard segments. The polyurea hard segments in 87- and 88- adhesives are harder and therefore have higher modulus than the MDI-butanediol polyurethane hard segments in the 73- adhesives even though the hard segment concentration in these polymers is less (see Fig. 5). The modulus of 88-2 is higher than 87-2 over the rubber plateau because of the higher concentration of hard segments in the 88-2 adhesive.

CONCLUSIONS

A family of segmented polyurethane adhesives called Halthanes has been developed at Lawrence Livermore National Laboratory. They were synthesized and characterized based on four structure-property relationships. The chemical structure of the prepolymer and curing agents controlled the cure properties of the adhesive. Adhesion was related to the polymer/substrate interface. Both mechanical and chemical adhesion play an important role in these segmented polyurethanes. The molecular architecture of the hard and soft segments determined the modulus and elastic properties of these adhesives. Tailoring the chemistry of the hard and soft segments produced a family of segmented polyurethanes of varying modulus and elasticity. If the requirement calls for high elasticity, the 73- adhesives can be used. If a stiffer adhesive is required, 87- or 88- series adhesives are used.

We are currently investigating the degradation behavior of these adhesives in weapons environments using temperature to accelerate the degradation. The adhesives have a tendency to yellow with age but retain their properties quite well. Since the Adiprene L-100/MOCA segmented polyurethane system has been used for years, we do not anticipate any problems in this area.

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Table I. 73-series prepolymer and curing agent formulations.

Component	14	15	18	19
	Curing Agents			
Polymeg 1000	90	90	85	85
1,4-butanediol	10	10	10	10
Quadrol	-	-	5	5
FAA	-	0.0156	-	0.0107
	Prepolymer			
Polymeg 1000	47.6	47.6	47.6	47.6
Polymeg 2000	7.4	7.4	7.4	7.4
MDI	45.0	45.0	45.0	45.0
Prepolymer: Curing agent	62/38	62/38	65/35	65/35

Table II. Prepolymer and curing agent formulations for polyurea hard segment adhesives.

Component	87-1	87-2	88-2
	Curing Agents		
Tonox 60/40	100	-	-
XU-205	-	100	100
	Prepolymer		
Polymeg 2000	77.6	77.6	74.0
HMDI	22.4	22.4	26.0
Prepolymer: Curing agent	93/7	92/8	88/12

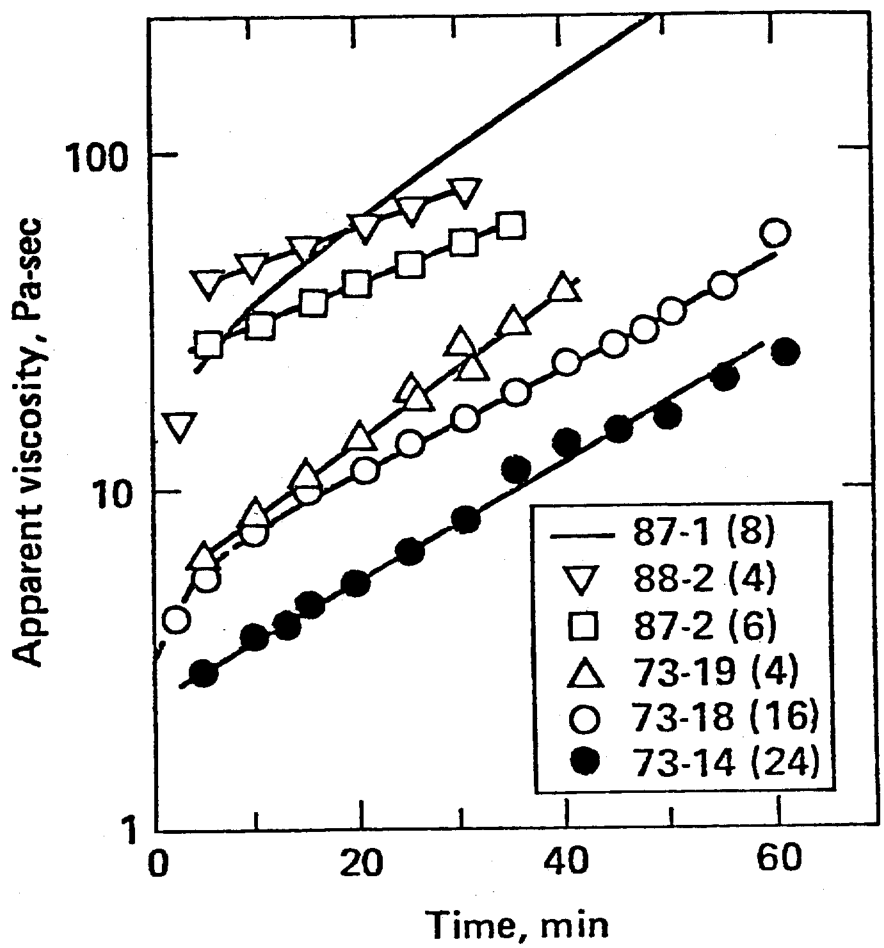

Fig. 1. The apparent viscosity of Halthane adhesives increases exponentially with curing time.

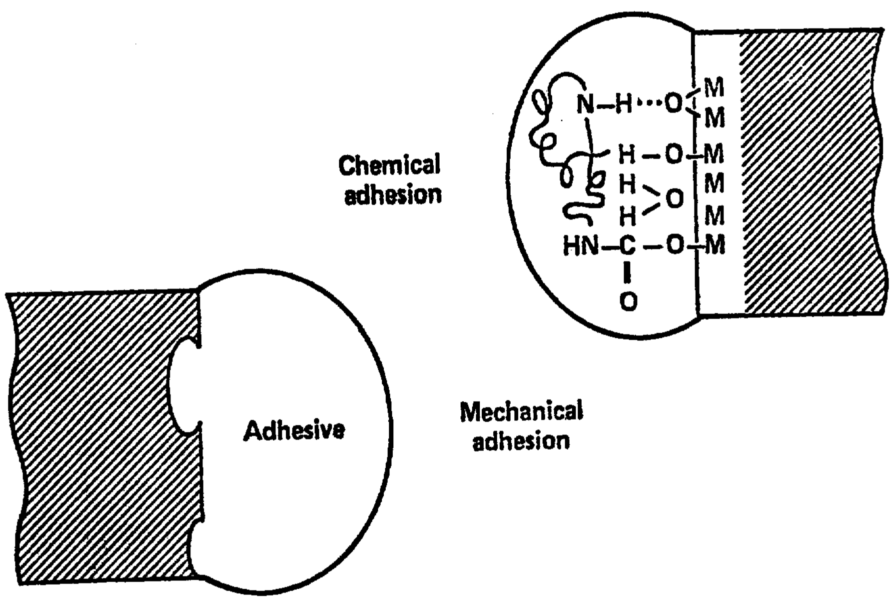

Fig. 2. Schematic representations of chemical and mechanical interactions occuring at the adhesive-substrate interface.

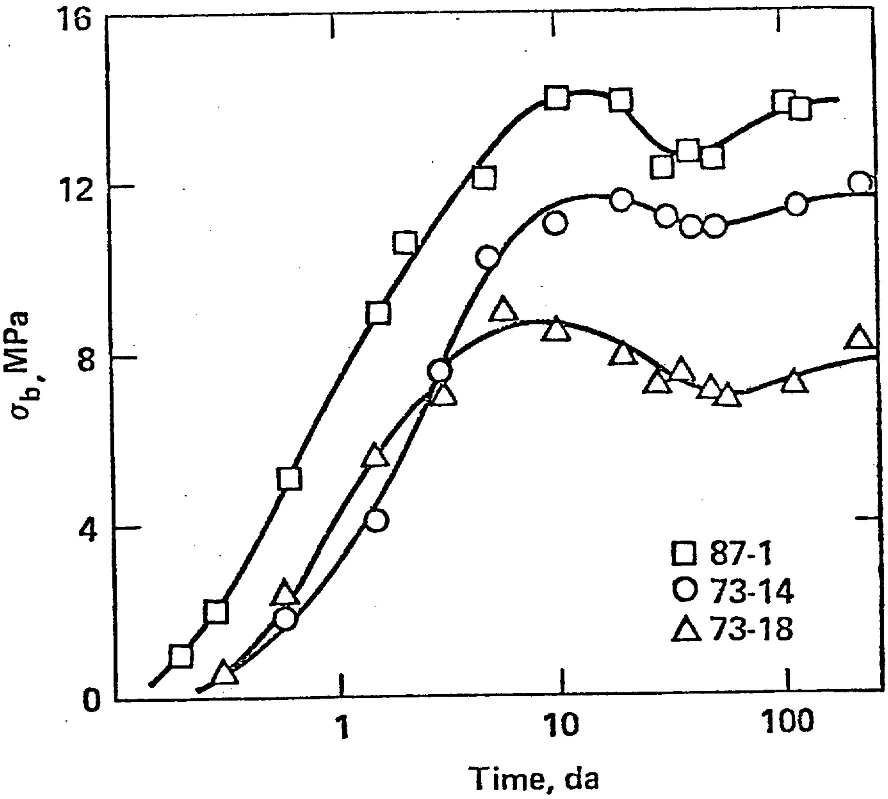

Fig. 3. The butt-tensile strength of Halthanes 73-14, 73-18, and 87-1 bonded to aluminium depends on both mechanical and chemical interactions at the adhesive-substrate interface.

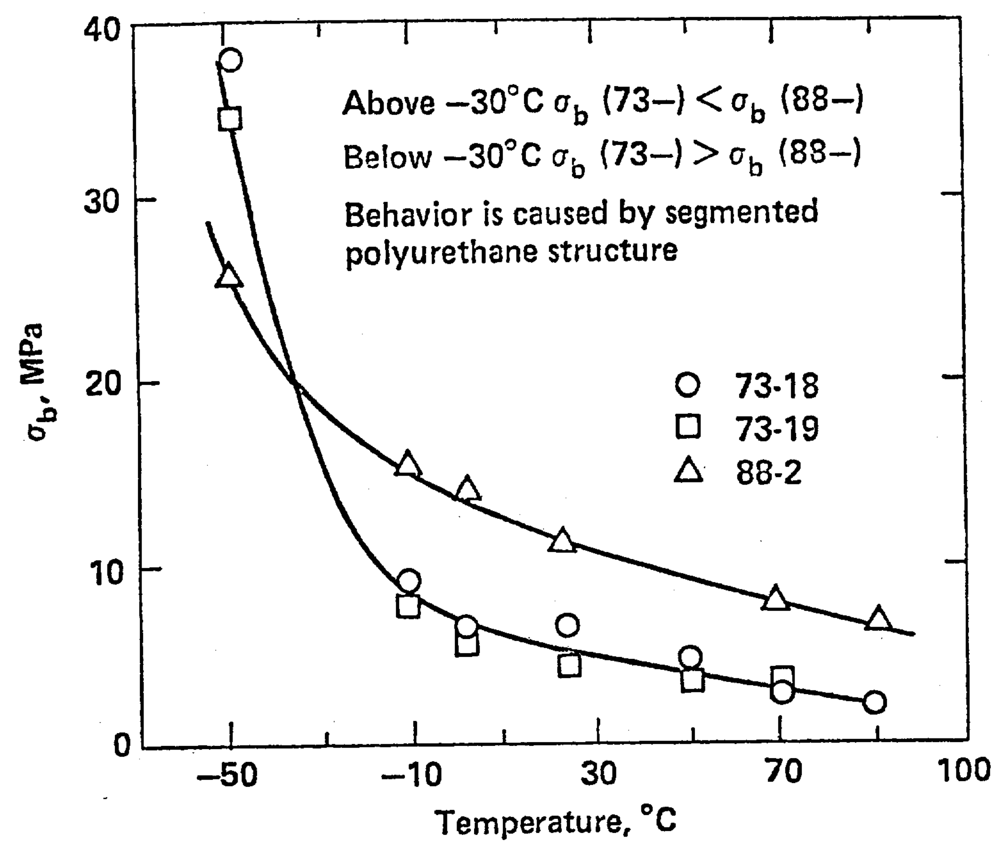

Fig. 4. The effect of mechanical interactions at the adhesive interface is shown in the rapid increase in butt-tensile strength of the Halthane adhesives as the soft segment glass transition is approached.

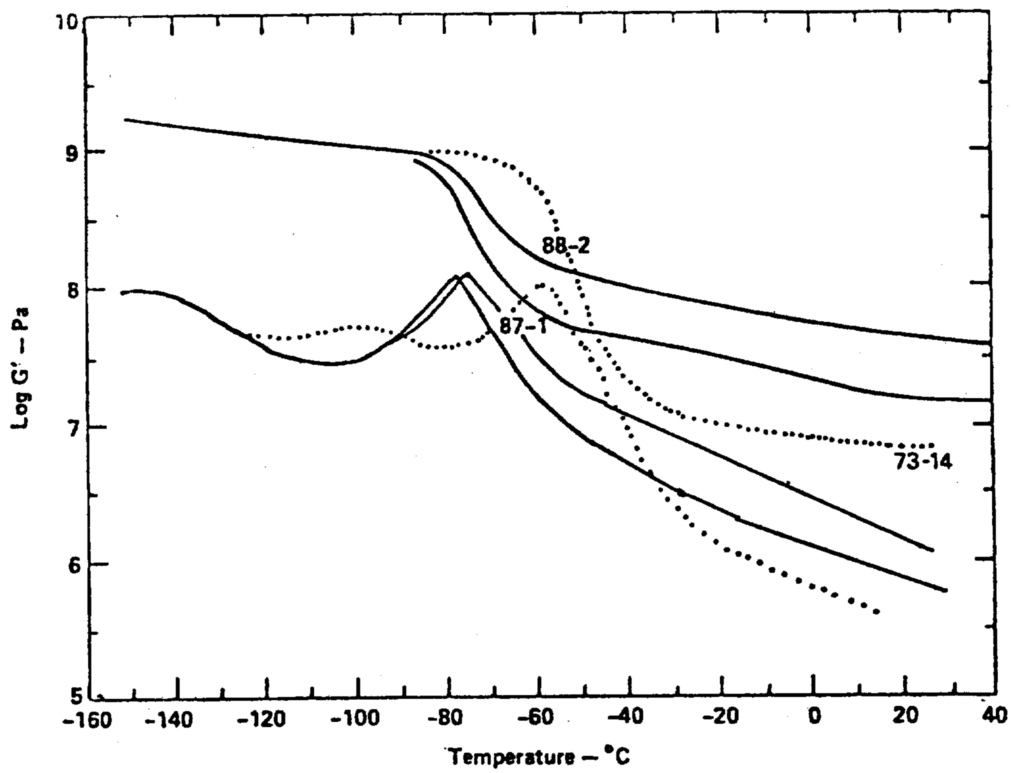

Fig. 5. Peaks in the loss modulus (G") in the low temperature dynamic mechanical spectrum indicate that the soft segment glass transition of the low molecular weight polyols in 73-14 occurs at -55°C while in the higher molecular weight polyols of the 87- and 88- adhesives the glass transition occurs at -79°C at 0.1 Hz.

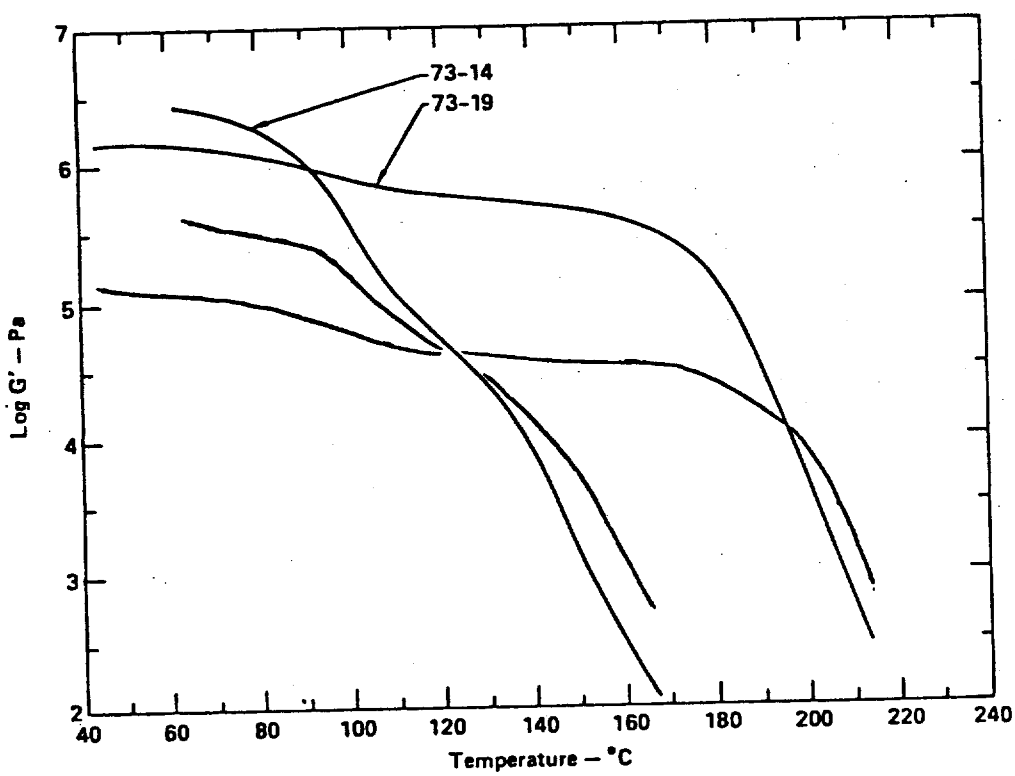

Fig. 6. The high temperature dynamic mechanical specturm of 73-14 and 73-19 shows the improvement in mechanical properties due to incorporation of the tetrafunctional curing agent quadrol in the 73-19 Halthanes.

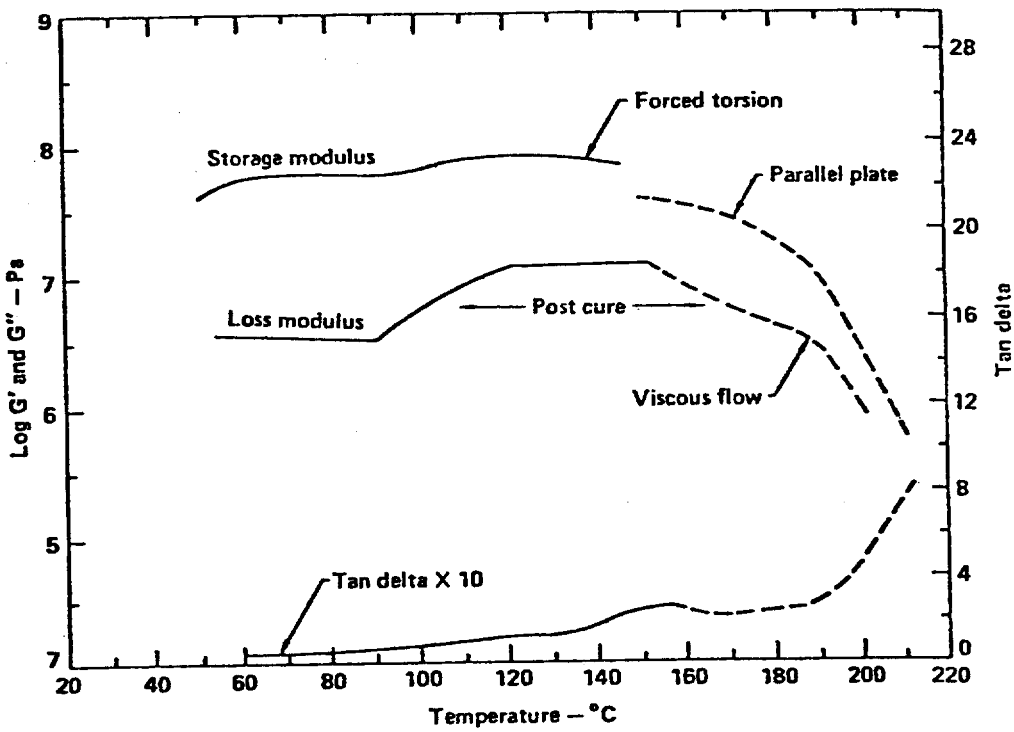

Fig. 7. The high temperature dynamic mechanical spectrum of 88-2 shows further curing of the hard segments occuring above 100°C. The onset of viscous flow above 200°C indicates that T_g(HS) has been exceeded.